

CLAIMS:

What is claimed is:

1. A catalyst composition that is the reaction product of
 - (a) an organometallic catalyst compound having
 - (i) at least one stabilizing ligand, and
 - (ii) at least one labile ligand suitable for olefin insertion and abstractable to form an active metal center; and
 - (b) a cocatalyst compound comprising
 - (i) a cation that comprises a fluoroaryl-ligand-substituted secondary amine or phosphine, wherein the aryl moiety is one of phenyl, substituted phenyl, biphenyl, substituted biphenyl, terphenyls and substituted terphenyls; and
 - (ii) an anion that comprises a Group-13 element, wherein the anion is substantially noncoordinating.
2. The catalyst composition of claim 1 wherein the cocatalyst compound is represented by the formula:
$$[R'_iArF\cdot ER_2\cdot H]^+ [(M')Q_1Q_2\dots Q_n]^-, \text{ where}$$
 - (a) ArF is a fluoroaryl ligand;
 - (b) E is nitrogen or phosphorous;
 - (c) each R is independently a C₁-C₂₀ hydrocarbyl or hydrocarbysilyl group, or two R's may connect to form an unsubstituted or substituted C₂-C₂₀ cycloaliphatic group;
 - (d) R' is a C₁-C₂₀ hydrocarbyl or halogenated hydrocarbyl;
 - (e) i is 0, 1 or 2;
 - (f) M' is at least one Group-13 element;
 - (g) n is at least one; and
 - (h) Q connect to M and are selected to render [(M')Q₁Q₂...Q_n]⁻ substantially noncoordinating.
3. The catalyst composition of claim 2 wherein each Q ligand comprises at least one fluorinated aryl group, or at least one substituted aryl group wherein the substitutions comprise fluorinated hydrocarbyl groups.
4. The catalyst composition of claim 3 wherein each Q ligand comprises 5 to 20 carbon atoms in a fused or pendant ring system.
- 35 5. The catalyst composition of claim 3 wherein each Q ligand is perfluorinated.

6. The catalyst composition of claim 2 or 3 wherein RⁱArF-ER₂ is selected
from N-pentafluorophenylpyrrolidine, N-para-nonafluoro-
biphenylpyrrolidine, N-tridecafluoroterphenylpyrrolidine, N-pentafluoro-
phenylpyrrole, N-paranonafluorobiphenylpyrrole, N-tridecafluoro-
terphenylpyrrole, N-pentafluorophenylpiperidine, N-paranonafluoro-
biphenylpiperidine, N-tridecafluoroterphenylpiperidine, N-pentafluoro-
phenylindoline, N-paranona-fluorobiphenylindoline, N-tridecafluoro-
terphenylindoline, N-pentafluorophenylindole, N-paranonafluoro-
biphenylindole, N-tridecafluoroterphenylindole, N-pentafluorophenyl-
azetidine, N-paranonafluorobiphenylazetidine, N-tridecafluoroterphenyl-
azetidine, N-pentafluorophenylaziridine, N-paranonafluoro-
biphenylaziridine, and N-tridecafluoroterphenylaziridine.

10 7. The catalyst composition of claims 1, 2, 3, 4, or 5 wherein the catalyst
compound is a Group-3-11 compound activatable for olefin polymerization
to a cation.

15 8. The catalyst composition of claim 6 wherein the catalyst compound is a
Group-3-11 compound activatable for olefin polymerization to a cation.

9. The catalyst composition of claim 7 wherein the catalyst compound is a
Group-3-6 metallocene having the formula:
20 $L^A L^B L^C_i MDE$ where:

25 (a) L^A connects to M and is a substituted or unsubstituted,
cyclopentadienyl or heterocyclopentadienyl ligand;

(b) L^B connects to M and is a substituted or unsubstituted,
cyclopentadienyl or heterocyclopentadienyl or is a heteroatom
ligand;
wherein L^A and L^B optionally connect together through a linking
group comprising a Group-14 element;

30 (c) L^C_i is an optional neutral, non-oxidizing ligand connected to M (i
equals 0 to 3);

(d) M is a Group-3-6 metal; and

(e) D and E are labile ligands that connect to M, and optionally
connect to each other, to L^A, or L^B,

wherein D or E are abstractable as a monoanion from M by the cocatalyst complex and wherein a monomer or polymerizable macromer can insert into M-D or M-E for polymerization.

10. The catalyst composition of claim 9 wherein M is titanium and L^B is a heteroatom connected to M.

5 11. The catalyst composition of claim 9 wherein M is zirconium or hafnium and L^B is a substituted or unsubstituted, cyclopentadienyl or heterocyclopentadienyl ligand connected to M.

12. A catalyst system for olefin polymerization comprising:

10 (a) an organometallic catalyst cation having at least one stabilizing ligand and a labile ligand suitable for olefin insertion wherein the catalyst cation is activated for olefin polymerization;

(b) a neutral, fluoroaryl-ligand-substituted secondary amine or phosphine; and

15 (c) a Group-13 substantially noncoordinating anion.

13. A catalyst according to claim 12 having a feature as recited in any of claims 2, 3, 4, 5, or 12.

14. A process for preparing polyolefins from one or more monomers comprising combining the monomers under polymerization conditions with an olefin polymerization catalyst that is the reaction product of

20 (a) an organometallic catalyst compound having at least one stabilizing ligand and at least one labile ligand suitable for olefin insertion and abstractable to leave a cationic metal center; and

(b) a Group-13-based cocatalyst complex comprising

25 (i) a cation having a protonated, fluoroaryl-ligand-substituted secondary amine or phosphine and

(ii) a substantially noncoordinating anion.

15. The process of claim 14 wherein the cocatalyst complex is represented by the formula:



30 (a) ArF is a fluoroaryl ligand,

(b) E is nitrogen or phosphorous,

5 (c) each R is independently a C₁-C₂₀ hydrocarbyl or hydrocarbysilyl group, or the two R's may connect to form an unsubstituted or substituted, C₂-C₂₀ cycloaliphatic group;

(d) R' is a C₁-C₂₀ hydrocarbyl or halogenated hydrocarbyl;

(e) i is 0, 1 or 2;

(f) M is at least one Group-13 element; and

(g) Q connect to M and are selected to render [(M')Q₁Q₂ . . . Q_n] substantially noncoordinating.

10 16. The process of claim 15 wherein Q comprise fluorinated aryl groups or comprise aryl groups having fluorinated hydrocarbyl substituents.

17. The process of claim 15 or 16 wherein R';ArF-ER₂ is selected from N-pentafluorophenylpyrrolidine, N-para-nonafluorobiphenylpyrrolidine, N-tridecafluoroterphenylpyrrolidine, N-pentafluorophenylpyrrole, N-paranonafluorobiphenylpyrrole, N-tridecafluoroterphenylpyrrole, N-pentafluorophenylpiperidine, N-paranonafluorobiphenylpiperidine, N-tridecafluoroterphenylpiperidine, N-pentafluorophenylindoline, N-paranona-fluorobiphenylindoline, N-tridecafluoroterphenylindoline, N-pentafluorophenylindole, N-paranonafluorobiphenylindole, N-trideca-fluoroterphenylindole, N-pentafluorophenylazetidine, N-paranonafluorobiphenylazetidine, N-tridecafluoroterphenylazetidine, N-pentafluoro-phenylaziridine, N-paranonafluorobiphenylaziridine, and N-tridecafluoro-terphenylaziridine.

18. The process of claims 14-16 wherein the catalyst compound is a Group 3-11 compound activatable to a cation for olefin polymerization.

25 19. The process of claim 17 wherein the catalyst compound is a Group 3-11 compound activatable to a cation for olefin polymerization.

20. The process of claim 18 wherein the catalyst compound is a Group 3-6 metallocene having the formula:

L^AL^BL^C_iMDE where

30 (a) L^A connects to M and is a substituted or unsubstituted cyclopentadienyl or heterocyclopentadienyl ligand;

5 (b) L^B connects to M and is a substituted or unsubstituted, cyclopentadienyl or heterocyclopentadienyl ligand or a heteroatom ligand; wherein the L^A and L^B ligands may connect through a linking group comprising a Group-14 element;

10 (c) L^C ; is an optional neutral, non-oxidizing ligand connected to M (i equals 0 to 3);

(d) M is a Group 3-6 metal; and,

15 (e) D and E are labile ligands, that connect to M, wherein the cocatalyst complex can abstract D or E and a monomer or polymerizable macromer can insert into M-D or M-E for polymerization; wherein D and E optionally connect to each other, to L^A , or L^B .

21. The process of claim 20 wherein M is titanium and L^B is a heteroatom connected to M.

15 22. The process of claims 20 wherein M is zirconium or hafnium and L^B is a substituted or unsubstituted, cyclopentadienyl or heterocyclopentadienyl connected to M.

20 23. The process of any of claims 14-16 wherein the olefin polymerization conditions comprise a solution, supercritical pressure, bulk, slurry, or gas-phase process conducted at temperatures from greater than or equal to 30 °C to less than or equal to 300 °C and pressures from greater than or equal to 0 to less than or equal to 2000 bar.

25 24. The process of claim 23 wherein the process is an adiabatic solution process conducted at a temperature greater than or equal to 40 °C to less than or equal to 250 °C.

25 25. The process of claim 23 wherein the process is bulk, slurry, or gas phase, and the activated catalyst compound is carried on or affixed to a particulate support.

30 26. The process of any of claims 14-16 wherein the olefinic monomers are at least one of ethylene, C_3-C_{20} olefins, C_5-C_{20} diolefins, C_7-C_{20} vinyl

aromatic monomers, C₄-C₂₀ geminally disubstituted olefins or C₅-C₂₀ cyclic olefins.

27. Use of a cation having a fluoroaryl-ligand-substituted secondary amine or phosphine for preparing a Group-13-based cocatalyst complex comprising a substantially noncoordinating anion.

28. Use of a precursor for polyolefin preparation wherein the precursor comprises a Group-13-based cocatalyst complex comprising a cation having a fluoroaryl-ligand-substituted secondary amine or phosphine and a substantially noncoordinating anion.

29. Use of a precursor for making an olefin polymerization catalyst wherein the precursor comprises a Group-13-based cocatalyst complex comprising a cation having a fluoroaryl-ligand-substituted secondary amine or phosphine and a substantially noncoordinating anion.

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